Infrared Spectra and Molecular Configuration of Dimeric Carboxylic Acids

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Bull. Inst. Chem. Res., Kyoto Univ., Vol. 46, No. 5, 1968

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Received October 17, 1968

Infrared spectra of several carboxylic acids and their deuterated derivatives have been measured at various low temperature till liquid nitrogen temperature. Each of the characteristic bands of carboxylic group has been observed as a pair. A satisfactory explanation has been given for the splitting of the bands. It is concluded that the two kinds of configuration having different energies and spectra coexist in the crystalline state. The energy differences have been estimated to be 0.1~0.3 Kcal/mole from intensity ratio measurement of the pairs. Mixing ratios of the wave functions from the two configurations have been calculated using the modified Wall-Glockler potential function.

INTRODUCTION

It has been generally conceived that symmetry operation of a crystal leads to configuration indistinguishable from the original one. Molecular configuration shown in Fig. 1 (A).[1] Symmetry of crystal requests that there exists only one kind of configuration, for example *cis* configuration.

On the other hand, from the stand point of statistical popuration, *trans* configuration shown in Fig. 1 (B) may be expected to coexist, if the difference of the free energies between *cis* and *trans* configuration is small. This expection is not comparible with consideration of symmetry of a crystal.

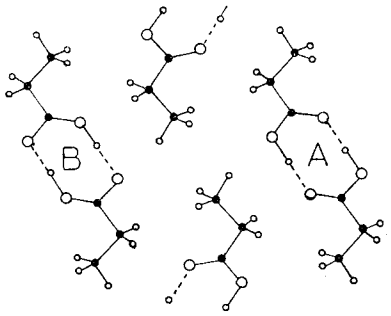

Fig. 1. Two kinds of configurations of propionic acid.

Splittings of characteristic bands and molecular configuration of benzoic acid dimmer have been discussed in a previous paper.[2] It has been concluded that the two kinds of configuration having different energies coexist in crystalline state.

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The difference is caused by inter-molecular interaction with neighbouring molecules, but not by intramolecular interaction, because two kinds of configurations are equivalent each other for isolated dimmer.

In the case of crystals of fatty acids, however, difference of energies between *cis* and *trans* configuration should be caused by intramolecular interaction together with intermolecular interaction, because the two configurations are nonequivalent each other.

In order to investigate the problem, infrared spectra of several carboxylic acids and their deuterated derivatives were observed at low temperature at which the fine structure of the bands can be measured.

EXPERIMENTAL

The purest grade of several commercial fatty acids were used without further purification. The deutero-carboxylic acids were prepared by hydrolysis of acid anhydride with deuterium oxide, or by repeated recrystalizations from acetone-deuterium oxide solution. Infrared spectra were measured by a Perkin Elmer 521 spectrophotometer.

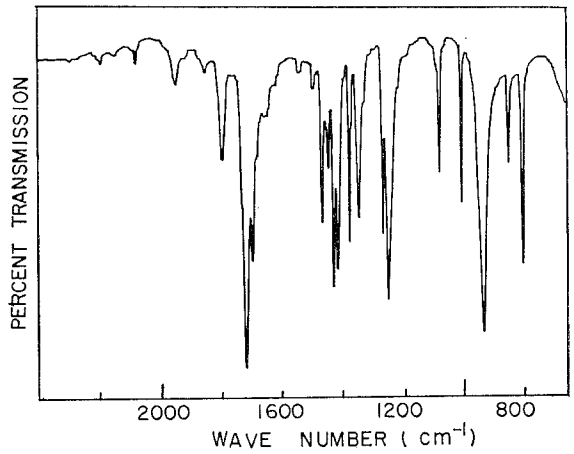

Fig. 2. Infrared spectra of propionic acid at −160°C.

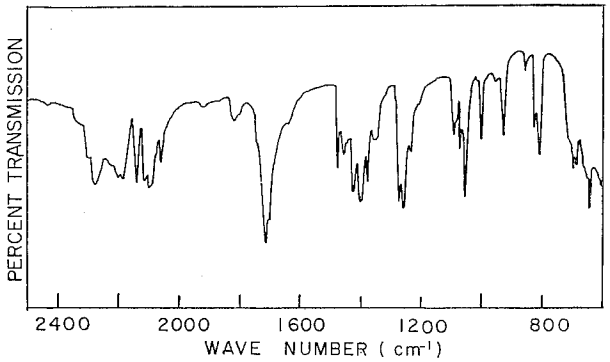

Fig. 3. Infrared spectra of d-propionic acid at −130°C.

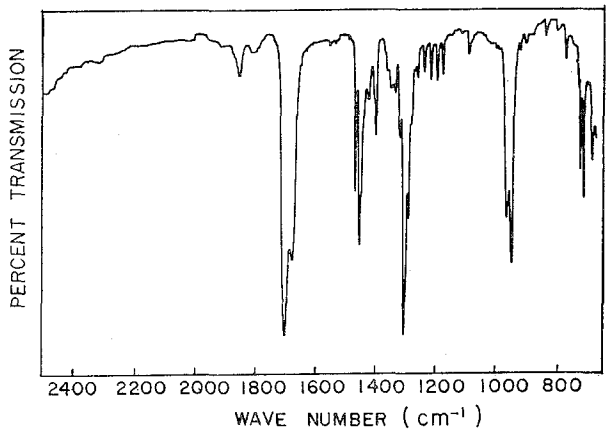

Fig. 4. Infrared spectra of palmitic acid at −140°C.

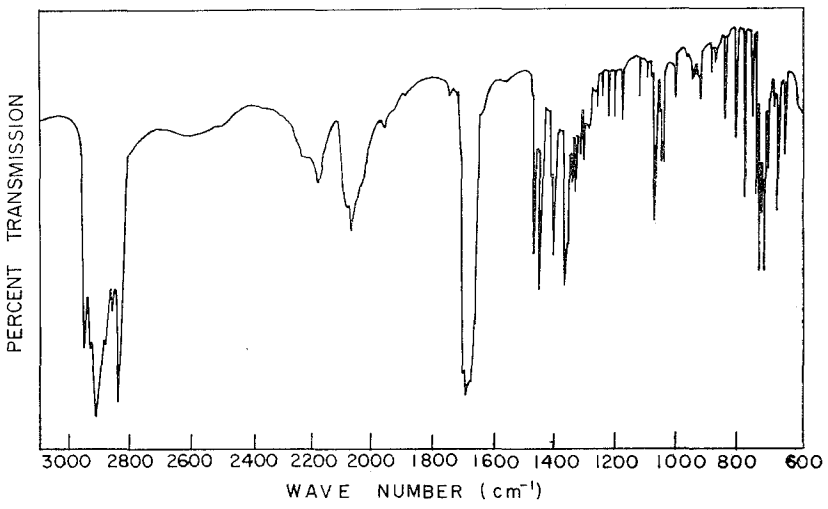

Fig. 5. Infared spectra of d-palmitic acid at −120°C.

RESULTS AND DISCUSSION

The infrared spectra of the fatty acids at low temperature are shown in Figs. 2∼5. It should be noticed that almost all characteristic bands of carboxylic group, those are C=O stretching mode at *ca.* 1700 cm^{-1}, mixing modes of C−O stretching and OH bending at *ca.* 1430 and 1300 cm^{-1}, and OH out-of-plane bending vibration at *ca.* 950 cm^{-1}, consist of two peaks.

The infrared spectra of deuterated compounds at low temperature show splitting of OD stretching, C=O stretching, C−O stretching, and OD in plane and out-of-plane bending vibrations.

Assignments of characteristic bands of carboxyl group are listed in Table 1. First column show alkil group of fatty acids, second cloumn kind of configuration, third to sixth frequencies of undeuterated compounds, and the remaining those of deuterated compound. It can be seen that almost all of characteristic bands of

Table 1. Assignment of characteristic bands of carboxyl group.

R-		νC=O	νC−O+δOH		σOH	νOD	νC=O	νC−O	δOD	σOD
$CH_3(CH_2)_{16}$-	A	1683	1428	1312	975	2080	1676	1378	1086	
	B	1698		1297	957	2200	1702	1368	1079	705
$CH_3(CH_2)_{14}$-	A	1682	1434	1312	976	2080	1682	1370	1084	722
	B	1696	1428	1297	959	2200	1696	1362	1074	706
$CH_3(CH_2)_{12}$-	A	1678	1428	1311	973	2075	1676	1378	1072	728
	B	1701		1293	956	2200	1702	1363	1050	705
$CH_3(CH_2)_{10}$-	A	1679	1428	1310	973	2080	1692	1374	1068	748
	B	1700		1298	956	2220	1704	1360	1053	705
$CH_3(CH_2)_9$-	A	1682	1443	1315	925	2102		1427	1081	696
	B	1700		1310	910	2235			1057	
$CH_3(CH_2)_8$-	A	1680	1428	1303	974	2080	1689	1373	1082	
	B	1700		1291	952	2200	1701	1340	1050	705
$CH_3(CH_2)_7$-	A	1681	1444	1313	925	2110	1682	1425	1081	698
	B	1700	1438	1308	913	2255	1695		1056	
$CH_3(CH_2)_6$-	A	1680	1430	1302	973		1685	1372	1086	736
	B	1698	1428	1290	952		1702	1345	1056	706
$CH_3(CH_2)_5$-	A	1682	1444	1340	924					
	B	1698		1307	913					
$CH_3(CH_2)_4$-	A	1682	1428	1311	945	2197	1688	1346	1075	703
	B	1695		1295	924	2240	1696		1068	650
$CH_3(CH_2)_3$-	A	1710	1425	1342	950	2108	1683	1408	1083	705
	B	1720		1287	915	2200	1708	1300	1056	653
$CH_3(CH_2)_2$-	A	1694	1440	1323	955					
	B	1708		1310						
$CH_3(CH_2)$ -	A	1719	1430	1346	852		1710	1397	1087	638
	B	1698	1415	1246	935		1696	1256	1053	692

various fatty acids consist of two peaks.

Corish and Chapman[3] have also observed that the absorption band of C=O stretching vibration consists of two peaks at low temperature. Bratož, Hadži and Sheppard[4] have observed that the absorption bands of OD stretching vibrations of many kinds of deuterated carboxylic acids consists of two peaks.

Many types of interpretations of these splittings were discussed in a previous paper.[1] The same conclusion is obtained again, that is the two kinds of configuration coexist in the crystal.

Figure 6 shows the potential energy curve of a dimer of fatty acid in terms of OH in-phase stretching coordinate. The two potential minima are nonequivalent

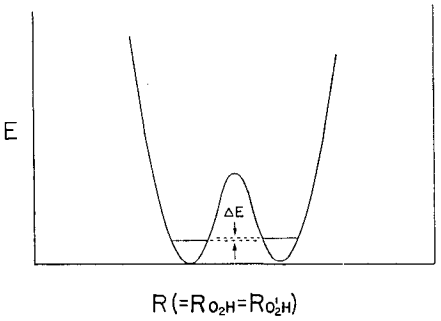

Fig. 6. Double minimum potential.

because of *cis* and *trans* configurations mentioned above. The lower left and the higher right potential minima correspond to the configuration (A) and (B) of Fig. 1, respectively.

If the two kinds of configuration coexist and the ratio of absorption coefficient of the pair is constant, the energy difference (ΔE) between two configurations (A) and (B) can be obtained from the following equation by measuring intensity ratios of the pair at various temperatures:

$$\ln\frac{A_B}{A_A}=\ln\left(\frac{K_B}{K_A}e^{\Delta S/R}\right)-\frac{\Delta E}{RT}$$

where A_A and A_B are the band areas for absorptions assigned to the configurations A and B, respectively, K_A and K_B the absorption coefficients of corresponding bands, and ΔS the difference of entropy between the two configurations A and B, Table 2 shows estimated values of the energy differences for various fatty acids.

Table 2. Energy differences between two kinds of configuration.

Compound	Band	Energy Difference (Kcal/mol)
$CH_3(CH_2)_{16}COOH$	$\nu C=O$	0.3_0
$CH_3(CH_2)_{14}COOH$	$\nu C=O$	0.3_2
	$\sigma O-H$	0.2_8
$CH_2(CH_2)_{12}COOH$	$\nu C=O$	0.3_0
$CH_3(CH_2)_{10}COOH$	$\nu C=O$	0.2_8
$CH_3(CH_2)COOH$	$\nu C=O$	0.1_0

The conclusion given in classical expression, that is "coexisting of two kinds of configuration," will be discussed now quantum mechanically. The classical expression corresponds to the splitting of ground level by double minimum potential. The wave functions of the splitted levels may be expressed approximately as follows:

$$\Psi_{\pm}=N^{\pm}(\psi_a\pm\lambda_{\pm}\psi_b)$$

where $N_{\pm}$ is the normarizing constant, ψ_a and ψ_b the wave functions concerning the configurations A and B, respectively, and $\lambda_{\pm}$ the mixing ratio.

The mixing ratios of ground levels of the two configurations are calculated for a simplified model, which is modified Wall-Glockler potential function.[6]

The hamiltonian of the model is assumed to be

$$H=-\frac{h^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}k(x-l)^2+A \qquad x>0$$

$$H=-\frac{h^2}{2m}\frac{d^2}{dx^2}+\frac{1}{2}k(x+l)^2 \qquad x<0$$

where k is a force constant of OH stretching mode, m the mass of a hydrogen atom, $2l$ the distance between the two potential minima shown in Fig. 7.

The value of k used is 5 md/Å, which leads to OH stretching frequency at about 3000 cm^{-1}, l is 0.26, which is obtained from the O……O distance (2.64 Å)[2]

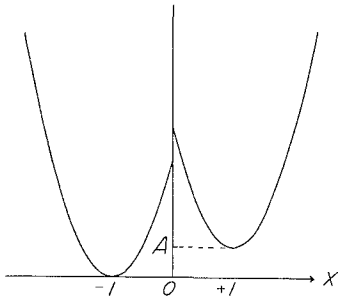

Fig. 7. Modified Wall-Glockler potential.

and OH bond length (1.06 Å).[7]

When A is 0.1 Kcal/mole

$$\Psi_+ = N_+\left(\psi_a + \frac{1}{3}\psi_b\right)$$

$$\Psi_- = N_+(\psi_a + \phi 3_b)$$

are obtained using the variation methods. Since probability is proportional to the square of λ, the mixing ratios of the configurations A and B are nine tenth, and one tenth, and *vice versa*. When A is 0.3 Kcal/mole, mixing is very small. Classical expression agreeds with quantum mechanical expression in these cases.

The nearly equal C−O distances of benzoic acid was interpreted as averages for mixture of two kinds of configuration.[1] The C−O distances of propionic acids obtained from x-ray analysis are 1.313 and 1.230 at −95°C, and 1.336 and 1.222 at 135°C.[2] Difference between two CO bond lengthes at lower temperature is larger than that at higher temperature. This result can be satisfactorily interpreted as change of popuration of the two kinds of configuration.

ACKNOWLEDGEMENT

The authers wish to thank Professor R. Gotoh and Dr. T. Takenaka for their kind advices and encouragement throughout this work.

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